

Final Report: Summary of Research for NASA ACPMAP NAG5-11297

Detailed Modeling and Analysis of the CPMF Dataset

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Research Objectives

A quantitative understanding of photolysis rate coefficients (or “ j -values”) is essential to determining the photochemical reaction rates that define ozone loss and other crucial processes in the atmosphere. j -Values can be calculated with radiative transfer models, derived from actinic flux observations, or inferred from trace gas measurements. The principal objective of this study is to cross-validate j -values from the Composition and Photodissociative Flux Measurement (CPFM) instrument during the Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) and SAGE III Ozone Loss and Validation Experiment (SOLVE) field campaigns with model calculations and other measurements and to use this detailed analysis to improve our ability to determine j -values. Another objective is to analyze the spectral flux from the CPMF (not just the j -values) and, using a multi-wavelength/multi-species spectral fitting technique, determine atmospheric composition.

Progress and Results

1. Improved Agreement of Modeled and Measured j -values in the Lower Stratosphere

This study begins with detailed comparisons of modeling and measurements made during the International Photolysis Frequency Measurement and Modeling Intercomparison (IPMMI). IPMMI was conducted during a one-week intensive at the Marshall field site of the National Center for Atmospheric Research (NCAR), near Boulder, Colorado, June 15–19, 1998, followed by analysis over several years [Cantrell *et al.*, 2003]. Twenty-one researchers from eight different institutions participated in the measurement portion of the intercomparison, and 18 modelers from 13 groups

Table 1. NO₂ cross sections and extraterrestrial solar flux used in initial and revised versions of the data

<i>j</i> -Value Source	NO ₂ Cross Section	ET Flux
APL radiative transfer model		
initial (POLARIS version)	<i>DeMore et al.</i> [1997]	MODTRAN
revised	<i>Harder et al.</i> [1997]	ATLAS
IPMMI spectroradiometer (<i>j</i>_{NO₂})		
initial (<i>DeMore et al.</i>)	<i>DeMore et al.</i> [1997]	—
revised (<i>Harder et al.</i>)	<i>Harder et al.</i> [1997]	—
CPFM spectroradiometer (<i>j</i>_{NO₂})		
initial (POLARIS)	<i>DeMore et al.</i> [1997]	—
revised (estimated)	<i>Harder et al.</i> [1997]	—

provided modeling calculations. The intercomparison focused on spectral actinic flux [*Bais et al.*, 2003] and the photolysis rate coefficients for NO₂, *j*_{NO₂} [*Shetter et al.*, 2003], and ozone photolysis to O(¹D), *j*_{O₃→O(¹D)} [*Hofzumahaus et al.*, 2004]. One of the major goals of IPMMI was to make recommendations as to which of the various model input data (e.g., extraterrestrial solar irradiance, absorption cross sections) lead to the greatest consistency between measurements and modeling calculations, based on the results of the intercomparison. Analysis was supported in part by this grant because of the significant impact the IPMMI findings have on the calculation of *j*-values using CPM data and the comparison of CPM *j*-values with both models and in situ measurements of NO_x partitioning.

The results described in the following paragraphs are summarized in Tables 1 and 2.

Extraterrestrial solar flux. A number of models in IPMMI used the ATLAS extraterrestrial solar spectrum [*Kaye and Miller*, 1996; *Woods et al.*, 1996]. The APL model, in contrast, used the MODTRAN3 spectrum [*Berk et al.*, 1989], as was used for the APL model–CPFM comparisons reported by *Swartz et al.* [1999] and *Del Negro et al.* [1999] during the POLARIS campaign. This difference led to some significant deviations from the other models and with actinic flux measurements at the ground. In particular, over 300–315 nm, where ozone photolysis occurs, the MODTRAN flux exceeds ATLAS by roughly 7%, with excursions of up to 20%. Thus, the selection of the solar spectrum alone increased APL modeled flux by several percent in this region, which is important for ozone photolysis.

The ATLAS-derived model calculations agreed better with the measured spectra at the ground during IPMMI, which suggests the superiority of the ATLAS spectrum for model calculations [*Swartz*, 2002; *Bais et al.*, 2003]. This also supports the recent general trend found in the literature toward using the ATLAS extraterrestrial flux [*Gröbner and Kerr*, 2001]. The ATLAS flux (290–420 nm) should be used in *j*-value modeling.

Support for larger NO₂ cross sections. All of the models used in IPMMI (including the APL model) utilized the *DeMore et al.* [1997] or comparable NO₂ cross sections, σ_{NO₂}. The models were compared to *j*_{NO₂} chemical actinometers in order to determine the absolute accuracy of the

Table 2. Summary of initial and revised j_{NO_2} and j_{O_3} relative agreement

j_{NO_2} (%) [initial \rightarrow revised values] ^a	j_{O_3} (%)	Comparison ^b	Solar Zenith Angle	Campaign
-14 \rightarrow -7	+7 \rightarrow <1	APL vs. actinometer ^c	16°–75°	IPMMI
+1	+8 \rightarrow +1	APL vs. spectroradiometer ^d	16°–75°	IPMMI
+9	+14 \rightarrow +7	APL vs. CPFM ^e	27°–85°	POLARIS
-5 \rightarrow +2	—	APL vs. $j_{\text{NO}_2,ss}$ ^f	27°–85°	POLARIS
-12 \rightarrow -5	—	CPFM vs. $j_{\text{NO}_2,ss}$ ^g	27°–85°	POLARIS

^aSee Table 1 for an explanation of the NO_2 cross sections and extraterrestrial solar flux used in the initial and revised versions of the data.

^bBased on scatter plots of the data, forced through the origin. When the APL model is compared with spectroradiometers, the same cross sections are used in both the model and spectroradiometer computations.

^cAPL model compared with University of Maryland j_{NO_2} chemical actinometer (measurements made by W. H. Swartz) and NCAR j_{O_3} actinometer measurements [Swartz, 2002; Shetter *et al.*, 2003; Hofzumahaus *et al.*, 2004].

^dAPL model compared with NCAR spectroradiometers [Swartz, 2002; Shetter *et al.*, 2003; Hofzumahaus *et al.*, 2004].

^eAPL-CPFM model (using CPFM measured surface albedo) compared with CPFM flux-derived j -values [Swartz *et al.*, 1999; Swartz, 2002].

^fAPL-CPFM model compared with steady-state j_{NO_2} , $j_{\text{NO}_2,ss}$, derived from observed NO , NO_2 , O_3 , ClO , and HO_2 [Del Negro *et al.*, 1999; Swartz, 2002].

^gCPFM compared with steady-state, measurement-derived j_{NO_2} [Del Negro *et al.*, 1999; Swartz, 2002].

size of the NO_2 cross sections. If a rough uncertainty of 10% for the model calculations is assumed [Shetter et al., 1992; Weihs and Webb, 1997], along with 7% for the actinometers, only nine of the 15 models used in IPMMI agree with the measured j_{NO_2} to within the combined model-measurement uncertainty [Swartz, 2002]. If larger NO_2 cross sections were used, however, like those of Harder et al. [1997], which lead to a j_{NO_2} of about 7% higher, all of the models would agree with the measurements to within the combined uncertainties, and eight of the models would agree to within the measurement uncertainty alone. This finding is consistent with the results of better IPMMI spectroradiometer-actinometer agreement when using the Harder et al. [1997] cross sections [Swartz, 2002; Shetter et al., 2003].

This conclusion also confirms results from the limited spectroradiometer-actinometer comparisons of Kraus et al. [2000], which showed better agreement when using the larger Mérianne et al. [1995] cross sections, in comparison with those of DeMore et al. [1997]. The community should thus consider using larger NO_2 cross sections [e.g., Mérianne et al., 1995; Harder et al., 1997] and/or further laboratory evaluations of σ_{NO_2} .

Implications of IPMMI findings for CPFM and POLARIS data. The results from the IPMMI intercomparison have important implications for the CPFM. Replacing the MODTRAN extraterrestrial flux with the ATLAS data reduces APL model j_{O_3} by about 7% on average. This impressive correction brought the APL model into nearly perfect average agreement with j_{O_3} chemical actinometer and spectroradiometer measurements during IPMMI. If the POLARIS j_{O_3} calculations [Swartz et al., 1999] were re-computed with the ATLAS extraterrestrial flux, the $\text{APL}_{\text{CPFM}}^1/\text{CPFM}$ agreement would go from +14% to about +7%, and the $\text{APL}_{\text{TOMS}}^1/\text{CPFM}$ agreement would drop from +8% to +1%, dramatically improving agreement with CPFM flux-derived j -values [Swartz, 2002].

Since both the APL model and CPFM used the same cross section for j_{NO_2} during POLARIS [Swartz et al., 1999], increasing σ_{NO_2} would not affect their agreement. However, Del Negro et al. [1999] compared modeled and CPFM-derived j_{NO_2} to steady-state j_{NO_2} , $j_{\text{NO}_2, \text{ss}}$, inferred from measured NO , NO_2 , O_3 , ClO , and HO_2 . Use of the larger Harder et al. [1997] NO_2 cross sections during POLARIS would increase the model and CPFM-derived j_{NO_2} , improving agreement with $j_{\text{NO}_2, \text{ss}}$. The same is true for $[\text{NO}_2]$ inferred from in situ trace gas measurements and modeled and CPFM j_{NO_2} —using larger NO_2 cross sections would significantly improve CPFM and APL agreement with the measured chemical composition along the ER-2 flight track.

We are currently preparing a manuscript for publication (Swartz, W. H., R. E. Shetter, L. A. Del Negro, and C. T. McElroy, “Improved agreement of modeled and measured j -values in the lower stratosphere,” in preparation), which will include our reevaluation of the POLARIS j -values, modeled, derived from CPFM, and inferred from in situ chemistry ($j_{\text{NO}_2, \text{ss}}$ from Del Negro et al. [1999]).

The high-solar zenith angle conditions during SOLVE posed a much greater challenge. Unfortunately, technical difficulties rendered the CPFM data from SOLVE ultimately not sufficiently tractable to warrant further detailed analysis of the CPFM j -value algorithm in the context of SOLVE. We thus turned our attention instead to the analysis of CPFM spectral flux data from POLARIS to support the development of a multi-wavelength/multi-species spectral fitting retrieval,

¹APL model calculations based on CPFM and TOMS column ozone and surface reflectivity data, APL_{CPFM} and APL_{TOMS} , are described by Swartz et al. [1999].

which would be of tremendous importance in analyzing datasets from new aircraft- and space-based platforms (e.g., OMI).

2. Multi-Spectral Retrieval of Ozone Column using CPFM Data

Overview. The CPFM spectrometer measures the direct attenuated solar irradiance across a horizontal diffuser plate on the top of the instrument [McElroy, 1995]. The density of the atmosphere and resultant scattering above ER-2 altitudes is very small. Thus, the measured irradiance, when cosine-corrected for the solar zenith angle, is essentially equal to the direct solar irradiance—assumed the total downwelling portion the radiation field. In this study we have used the upward-looking CPFM data to infer the ozone column between the instrument and the Sun. We have used standard least squares fitting techniques to perform this inversion. In order to do so, we constructed a forward model of the observations—that is, a functional relationship between the CPFM measurements and various free parameters, including the ozone column. Standard fitting routines were then used to determine the values of the free parameters most likely to produce the CPFM measurements.

Our ability to infer the ozone column is limited by the fidelity of the forward model. The model fidelity, in turn, is limited by our knowledge of the instrument, as well as various physical quantities such as the solar spectrum and the extinction cross sections involved. Our knowledge of the instrument is based on our collaboration with C. T. McElroy (Environment Canada). Our model of solar occultation is based on the stellar occultation work described by Yee *et al.* [2002] and DeMajistre and Yee [2002].

We will first describe the forward model, including both the occultation and instrument characterization. The retrieval method will then be explained.

Forward model. Each spectral element of the CPFM data, S_j , can be written as

$$S_j = A_j(\mathbf{u}) \int s(\lambda - \lambda_i) I(\lambda) d\lambda, \quad (1)$$

where $I(\lambda)$ is the directly transmitted solar radiance entering the CPFM instrument, $s(\lambda - \lambda_i)$ is the instrument spectral spread function, and $A_j(\mathbf{u})$ is the CPFM angular response, i.e., the sensitivity of the instrument for a given unit vector to the Sun, \mathbf{u} , measured in instrument coordinates. The solar radiance is independent of the instrument and is treated separately from the instrument functions $A_j(\mathbf{u})$ and $s(\lambda - \lambda_i)$ below.

Radiance model. The solar radiance entering the CPFM can be written as

$$I(\lambda) = I_\infty(\lambda) \exp \left(- \sum_k \int_0^\infty \sigma_k n_k ds \right), \quad (2)$$

where $I_\infty(\lambda)$ is the extraterrestrial solar irradiance, and σ_k and n_k are the extinction cross sections and corresponding densities for the constituents along the path to the Sun, ds . The constituents considered are (1) O_2 and N_2 (providing Rayleigh scattering), (2) ozone, (3) aerosols, (4) NO_2 , and (5) NO_3 . At some wavelengths for some constituents (including ozone), the cross section depends on the temperature and is therefore, strictly speaking, a function of position. We assume that the temperature measured on the aircraft is representative of the temperature for most of the

absorbing constituents along the path (this assumption will result in a small systematic error). We now write

$$I(\lambda) = I_{\infty}(\lambda) \exp\left(-\sum_k \sigma_k^* N_k\right), \quad (3)$$

where σ_k^* are the effective cross sections and N_k are the column densities for the constituents k . This is the forward model that we use for the radiance at the CPFM.

CPFM model. The instrument spectral spread function, $s(\lambda - \lambda_i)$, was provided by C. T. McElroy and has been used directly. The treatment of the spatial response, $A_j(\mathbf{u})$, is a bit more complicated. The intended design of the CPFM was to have the spatial response be proportional to $\cos \theta$, where θ is the solar zenith angle when the instrument is in its nominal orientation. To the extent to which this goal is met, the CPFM measurements are proportional to the downwelling hemispheric flux. For this reason, the CPFM data have been reported as

$$F_j = \frac{S_j}{C_j \cos \theta}, \quad (4)$$

where F_j is the downwelling flux and C_j is a calibration constant. To a small extent, however, this design goal was not met, particularly at longer wavelengths. The discrepancy is a rather complicated function of CPFM orientation for which a general characterization is not available. However, Tom McElroy has provided us with an estimate of the radiance for the September 21, 1997, flight where this effect has been accounted for. We have used this data set to calculate a revised hemispheric flux, F_j^* ,

$$F_j^* = \frac{1}{\cos \theta} \int s(\lambda - \lambda_i) I(\lambda) d\lambda, \quad (5)$$

which are the data used in the retrievals.

Retrieval. Combining (3) and (5), we can write

$$F_j^* = \frac{1}{\cos \theta} \int s(\lambda - \lambda_i) I_{\infty}(\lambda) e^{-\sum_k \sigma_k^* N_k} d\lambda. \quad (6)$$

We use a modified version of this equation in the retrieval in which we define the free parameters explicitly:

$$F_j^* = \frac{\alpha_0}{\cos \theta} \int s(\lambda - \lambda_i) I_{\infty}(\lambda) e^{-(\alpha_1 N_{\text{Ray}}^0 \sigma_{\text{Ray}}^* + \alpha_2 N_{\text{O}_3}^0 \sigma_{\text{O}_3}^* + \alpha_3 N_{\text{NO}_2}^0 \sigma_{\text{NO}_2}^* + \sum_k \sigma_k^* N_k)} d\lambda, \quad (7)$$

where the N^0 are climatological values of the column densities and the α_n are the free parameters to be retrieved. The summation in this equation employs climatological values of the other constituents along the path. The parameter α_0 when used in the retrieval accounts for forward model errors in calibration, aerosol extinction, and other factors that have a proportional effect on the corrected hemispheric flux. This final equation (7) is used in a standard Levenberg–Marquardt non-linear least squares fitting procedure. The results are reported below.

Results. The ER-2 transit flight from Fairbanks, Alaska to Barber's Point, Hawaii on September 21, 1997, was used for this analysis. Figure 1a shows the solar zenith angle and aircraft altitude along the flight track. In Figure 1b, the CPFM spectrum measured at the minimum solar zenith angle for the flight (35.6°), corrected for the "non-ideal" response of the diffuser plate, is shown, along with the best fit from the APL model. From this best fit the column ozone was inferred.

Figure 2 shows the retrieved ozone column throughout the flight. For comparison, the values retrieved by McElroy (C. T. McElroy, unpublished data) are also shown, along with the predicted ozone column. The ozone column was predicted assuming a horizontally homogeneous ozone field (profile based on ozonesonde data and scaled to the TOMS total ozone along the flight track [Swartz *et al.*, 1999]) and accounting for atmospheric refraction (based on 3-dimensional NCEP reanalysis data [Kalnay *et al.*, 1996]). The overall agreement is excellent, with the APL retrieval agreeing with our predicted column to within roughly 5%, except for the beginning of the flight. A number of factors may be causing discrepancies, including uncharacterized angular response of the CPFM diffuser and inaccuracies in the assumed ozone field (used for the predicted ozone column, including spatial inhomogeneities).

This multi-wavelength/multi-species spectral fitting retrieval based on CPFM data represents a preliminary effort. We are currently seeking opportunities to continue this work, analyzing CPFM and other multi-spectral datasets.

Summary

j-Value comparisons among models and measurements during IPMMI and POLARIS demonstrate the superiority of the ATLAS extraterrestrial solar spectrum (290–420 nm), which should be used for *j*-value modeling. Comparisons from IPMMI and POLARIS also show better agreement when using larger NO₂ cross sections [e.g., Harder *et al.*, 1997]. The community should thus consider using larger NO₂ cross sections and/or further laboratory evaluation of σ_{NO_2} . The use of the ATLAS extraterrestrial flux and larger NO₂ cross sections would remove a significant portion of the discrepancies of CPFM *j*-values with both the APL model and with measured NO_x partitioning during POLARIS (see initial and revised comparisons in Table 2). This also suggests that the algorithm currently used to convolve CPFM flux measurements and derive *j*-values is adequate for *j*-value calculation under POLARIS ER-2 conditions. We are currently preparing a manuscript for publication (Swartz, W. H., R. E. Shetter, L. A. Del Negro, and C. T. McElroy, "Improved agreement of modeled and measured *j*-values in the lower stratosphere," in preparation), which will include our reevaluation of the POLARIS *j*-values modeled, derived from CPFM, and inferred from in situ chemistry ($j_{\text{NO}_2, \text{ss}}$ from Del Negro *et al.* [1999]).

A preliminary multi-wavelength/multi-species spectral fitting retrieval analysis of the CPFM POLARIS data shows great promise, and we hope to apply it to other datasets (such as OMI) in the near future.

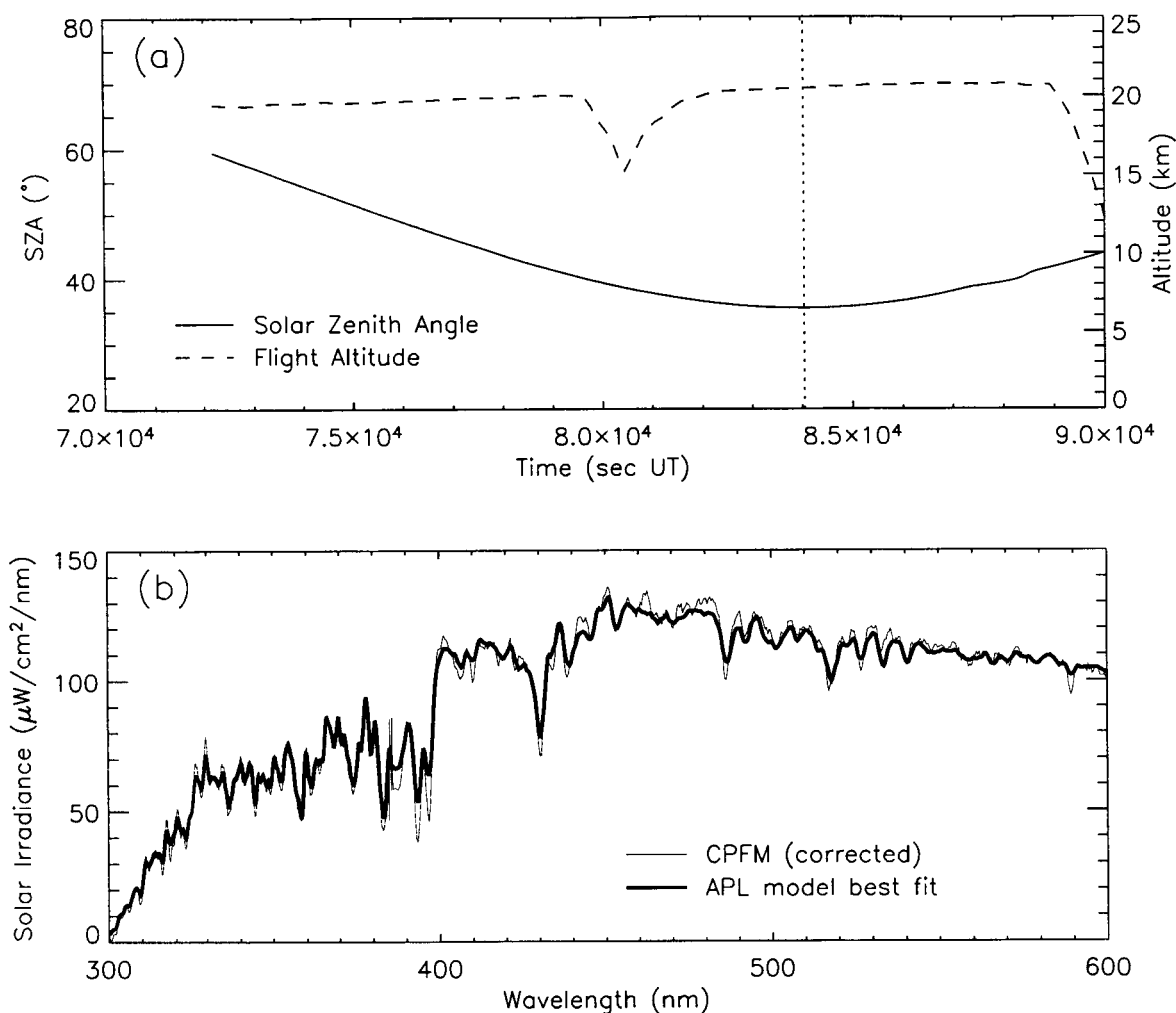


Figure 1. (a) Flight solar zenith angle (SZA) and ER-2 altitude for the September 21, 1997, transit flight from Fairbanks, Alaska to Barber's Point, Hawaii. The vertical dotted line represents the point of smallest SZA (35.6°), at $84,040$ sec UT. (b) Measured and model fitted solar irradiance spectra at $84,040$ sec UT ($\text{SZA}=35.6^\circ$). The CPFM measurements have been corrected for the "non-ideal" behavior of the CPFM diffuser plate, but not scaled by $\sec(\text{SZA})$. The best APL model fit of the spectrum is overlaid.

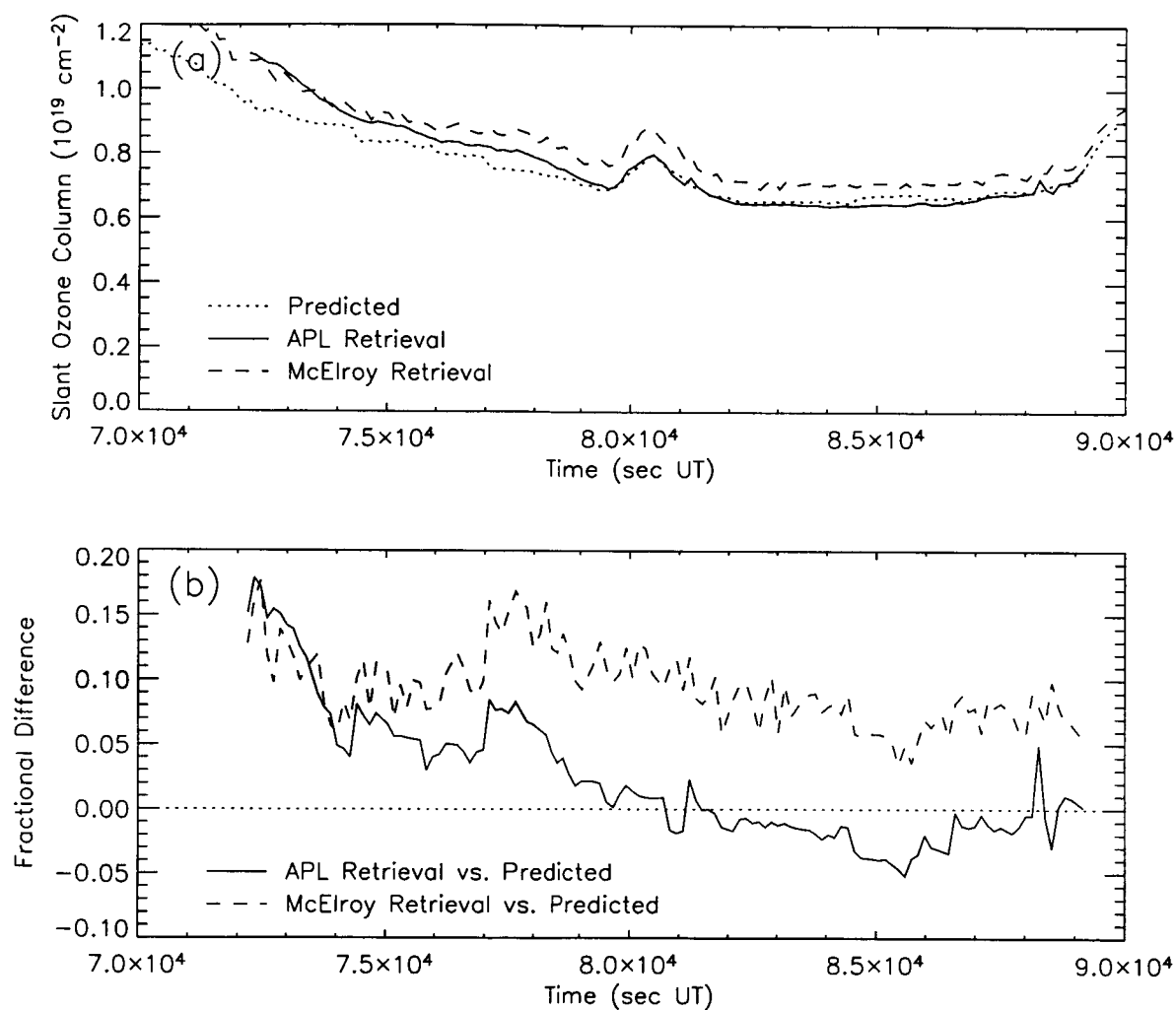


Figure 2. (a) Predicted and retrieved slant ozone column using the APL and McElroy retrievals. (b) The fractional difference between the two retrieval techniques and calculations: $(\text{retrieval}/\text{predicted}) - 1$.

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